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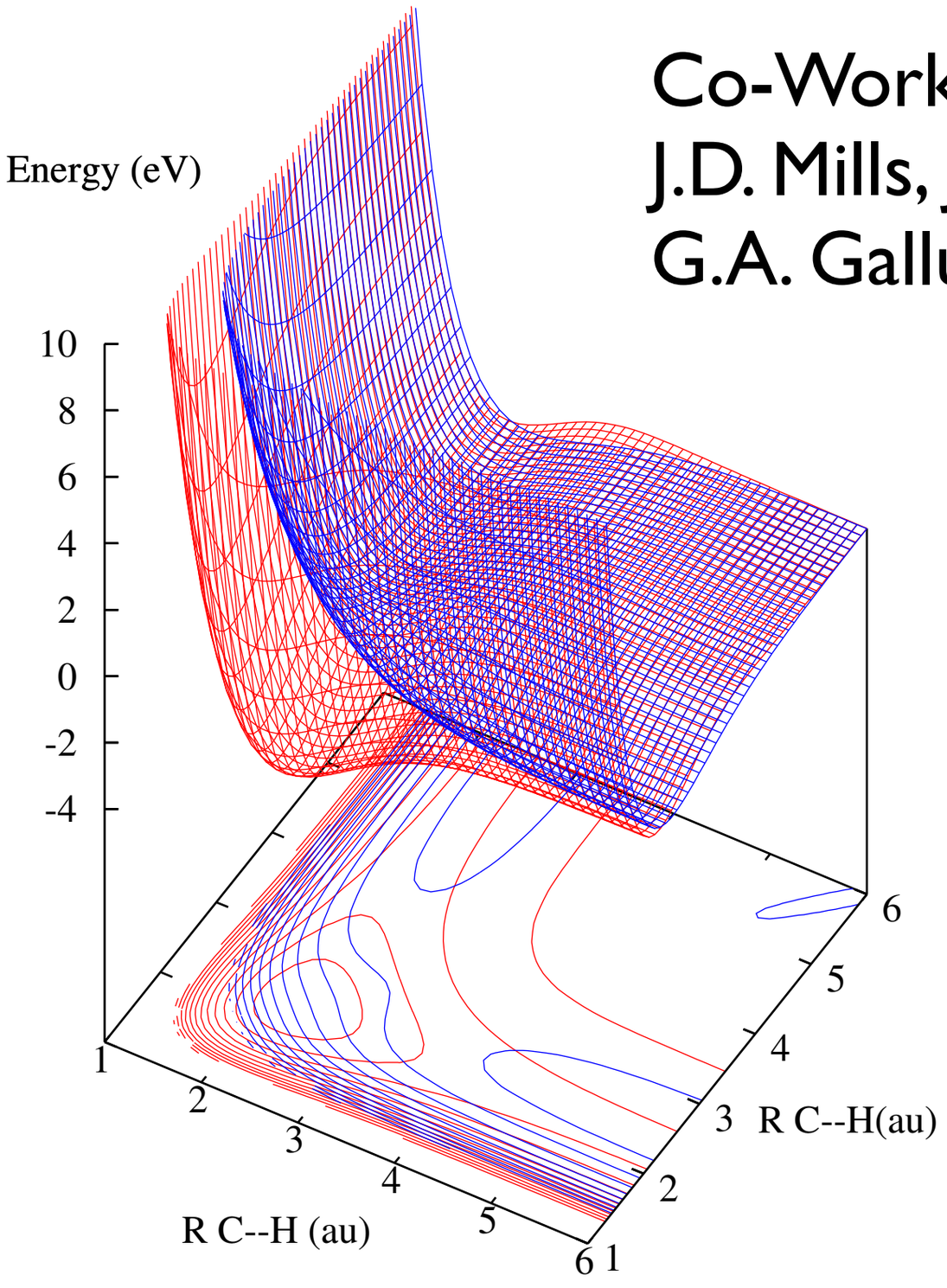
On the Question of Atoms and Bonds in Molecules

P.W. Langhoff, Chemistry & Biochemistry, UCSD



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50th Symposium on Theoretical Chemistry, University of Vienna, 14-18 September 2014

Selected Opinions on Atoms and Bonds in Molecules

"… there is a chemical bond when forces lead to formation of an independent molecular species…" Linus Pauling

"… a chemical bond is not a real thing – it is a figment of imagination which we have invented…" C.A. Coulson

"… attempts to regard a molecule as consisting of specific atoms or ionic units held together by discrete numbers of bonding electrons or electron pairs are considered as more or less meaningless…" R.S. Mulliken

"… that a molecule consists of atoms linked by a network of bonds is the cornerstone of chemical thinking…" R.F.W. Bader

"…the atom in a molecule is a vital, central chemical concept, yet forever elusive." - R.G. Parr, P.W. Ayers, and R.S. Nalewajski

"…our insights into the nature of atoms in molecules are still preliminary, and there is still much to learn…" K. Ruedenberg and W.H.E. Schwarz

“Molecules are made of atoms, aren’t they“… P.A.M. Dirac

When atoms form molecules their outer-valence orbitals melt…

Electronic charge is transferred among the atoms present…

The inner-valence atomic orbitals are also distorted to some extent…

Even core-level orbital energies are affected by molecular formation…

What is the central obstacle to making this picture quantitative, and how can we get around this obstacle?

“…since there is no specific assignment of the electrons occurring in the system to the nuclei involved, hence there are no atoms, isomers, conformations, etc…” - P.-O. Löwdin

“…there is no very fundamental difference between the van der Waals binding and covalent binding…” - J.C. Slater

Atomic Eigenstate Products as a Molecular Basis

$$\Phi(r:R) = \left\{ \Phi^{(1)}(1) \otimes \Phi^{(2)}(2) \otimes \cdots \Phi^{(N)}(n) \right\}_O$$

London, Eisenschitz,... van der Waals and covalent forces

Coulson, Moffitt,... atoms in molecules and crystals

Ellison, Tully, Kuntz,… diatomics in molecules

Hirschfelder, Claverie,... exchange perturbation theory

Karplus Festschrift,… PWL, J. Phys. Chem. **100**, 2974 (1996)

Some basic theory,… Chem. Phys. Letters **358**, 231 (2002)

Partitioning the Molecular Hamiltonian Operator

$$\hat{H}(\boldsymbol{r}:\boldsymbol{R}) = \sum_{\alpha=1}^{N} \hat{H}^{(\alpha)}(\boldsymbol{i}) + \sum_{\alpha=1}^{N-1} \sum_{\beta=\alpha+1}^{N} \hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})$$

$$\hat{H}^{(\alpha)}(\boldsymbol{i}) = \sum_{i}^{n_\alpha} \Big\{ -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{i'=i+1}^{n_\alpha} \frac{e^2}{r_{ii'}} \Big\}$$

$$\hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) = \frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}} - \sum_{i}^{n_\alpha} \frac{Z_\beta e^2}{r_{i\beta}} - \sum_{j}^{n_\beta} \frac{Z_\alpha e^2}{r_{j\alpha}} + \sum_{i}^{n_\alpha} \sum_{j}^{n_\beta} \frac{e^2}{r_{ij}}$$

$$= \hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) - \hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}\to\boldsymbol{\infty})$$

$$\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) \equiv \hat{H}^{(\alpha)}(\boldsymbol{i}) + \hat{H}^{(\beta)}(\boldsymbol{j}) + \hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})$$

Operators invariant under the subgroup $(S_{n_1} \otimes S_{n_2} \otimes \cdots S_{n_N})$ of S_{n_t}

Hamiltonian Matrix in the Atomic-Product Basis

$$\boldsymbol{H(R)} \equiv \langle \boldsymbol{\Phi(r:R)} | \hat{\boldsymbol{H}}\boldsymbol{(r:R)} | \boldsymbol{\Phi(r:R)} \rangle$$

$$= \sum_{\alpha=1}^{N} \boldsymbol{H}^{(\alpha)} + \sum_{\alpha=1}^{N-1} \sum_{\beta=\alpha+1}^{N} \boldsymbol{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$$

$$\boldsymbol{H}^{(\alpha)} = \left\{ \boldsymbol{I}^{(1)} \otimes \boldsymbol{I}^{(2)} \otimes \cdots \boldsymbol{E}^{(\alpha)} \otimes \cdots \boldsymbol{I}^{(N)} \right\}_o$$

$$\boldsymbol{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \left\{ \boldsymbol{I}^{(1)} \otimes \boldsymbol{I}^{(2)} \otimes \cdots \boldsymbol{V}_{\boldsymbol{d}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \otimes \cdots \boldsymbol{I}^{(N)} \right\}_o$$

$$\boldsymbol{V}_{\boldsymbol{d}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \equiv \langle \boldsymbol{\Phi}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) | \hat{\boldsymbol{V}}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) | \boldsymbol{\Phi}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) \rangle$$

Removing non-Pauli terms: J. Chem. Phys. **121**, 9323 (2004),

Theor. Chem. Acc. **120**,194 (2008), J. Phys. Chem. **113** 7687 (2009)

Universal Molecular Energy Expression

$$\Psi(r:R) \equiv \Phi(r:R) \cdot U_H(R)$$

$$E(R) \equiv {U_H}^{\dagger}(R) \cdot H(R) \cdot U_H(R)$$

$$= \sum_{\alpha=1}^{N} E^{(\alpha)}(R) + \sum_{\alpha=1}^{N-1} \sum_{\beta=\alpha+1}^{N} V^{(\alpha,\beta)}(R)$$

Atomic energy matrices:

$$E^{(\alpha)}(R) \equiv {U_H}^{\dagger}(R) \cdot H^{(\alpha)} \cdot U_H(R)$$

Bond energy matrices:

$$V^{(\alpha,\beta)}(R) \equiv {U_H}^{\dagger}(R) \cdot V^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot U_H(R)$$

Three Collinear and Triangular Hydrogen Atoms

Employ a four spin orbital basis for each atom - 1s, 2s

Construct the 64 x 64 **H**(R) matrix

Construct the physical part of the **U**(R) matrix

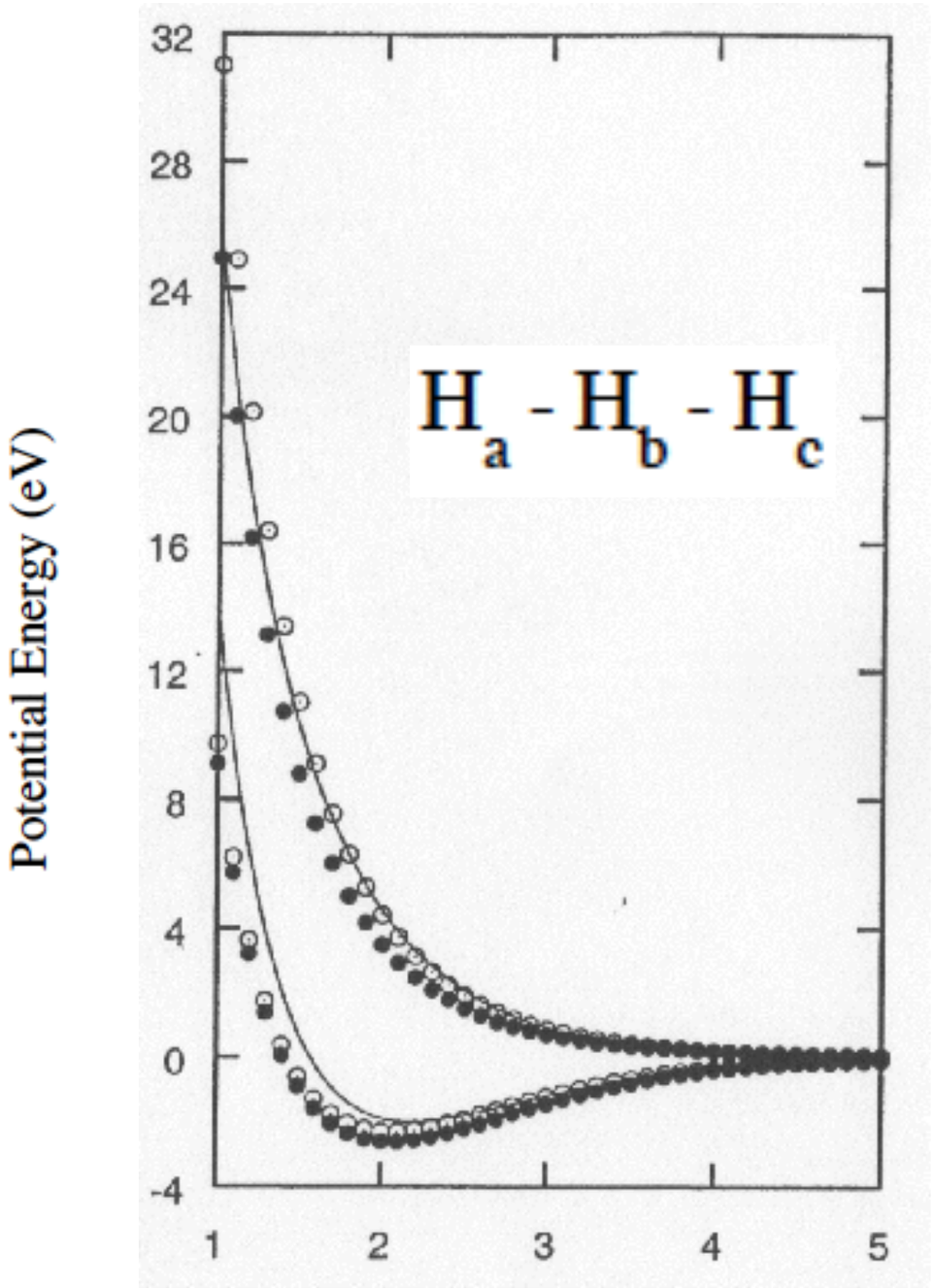
Evaluate the atomic energies and interaction potentials

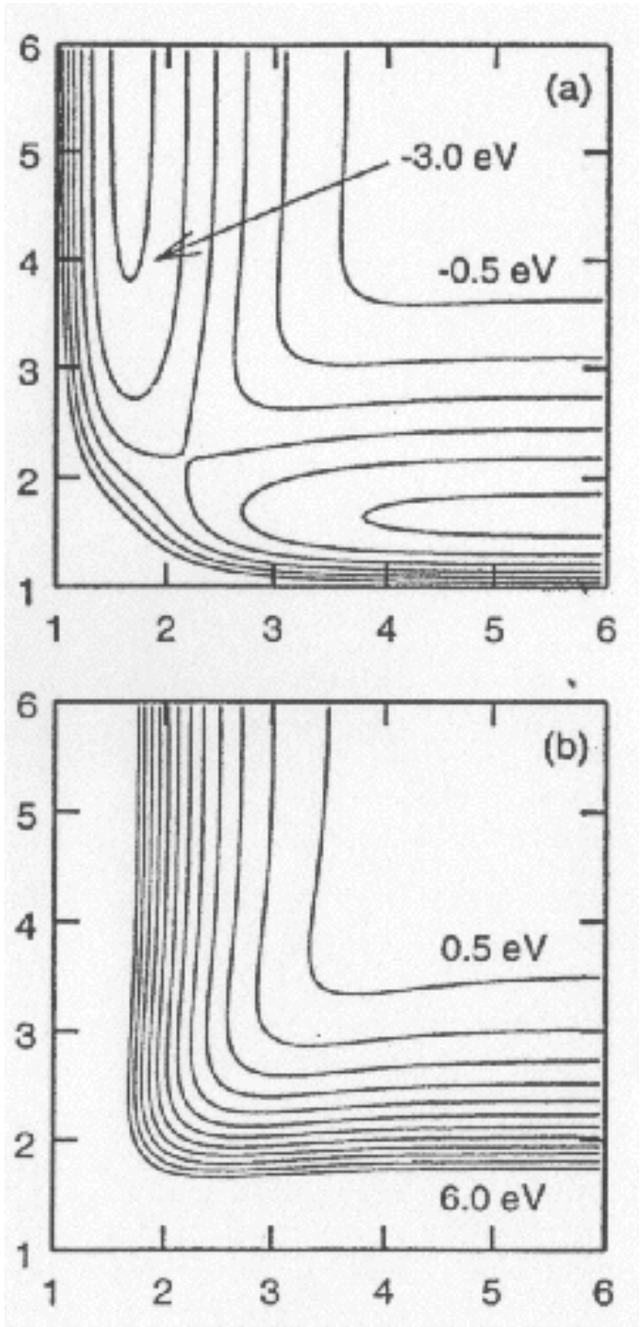
$$\tilde{E}_i^{(\alpha)}(\boldsymbol{R}) \equiv \{\tilde{\boldsymbol{E}}(\boldsymbol{R})\}_{ii} = \sum_{k=1}^{N_{sp}} \{\tilde{\boldsymbol{H}}^{(\alpha)}\}_{kk} \, |\{\tilde{\boldsymbol{U}}_{\boldsymbol{H}}(\boldsymbol{R})\}_{ki}|^2$$

$$\tilde{V}_i^{(\alpha,\beta)}(\boldsymbol{R}) = \sum_{k=1}^{N_{sp}} \{\tilde{\boldsymbol{E}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) - \tilde{\boldsymbol{E}}^{(\alpha,\beta)}(\infty)\}_{kk} \, |\{\tilde{\boldsymbol{U}}_{\boldsymbol{H}}{}^{(\alpha,\beta)}(\boldsymbol{R})\}_{ki}|^2$$

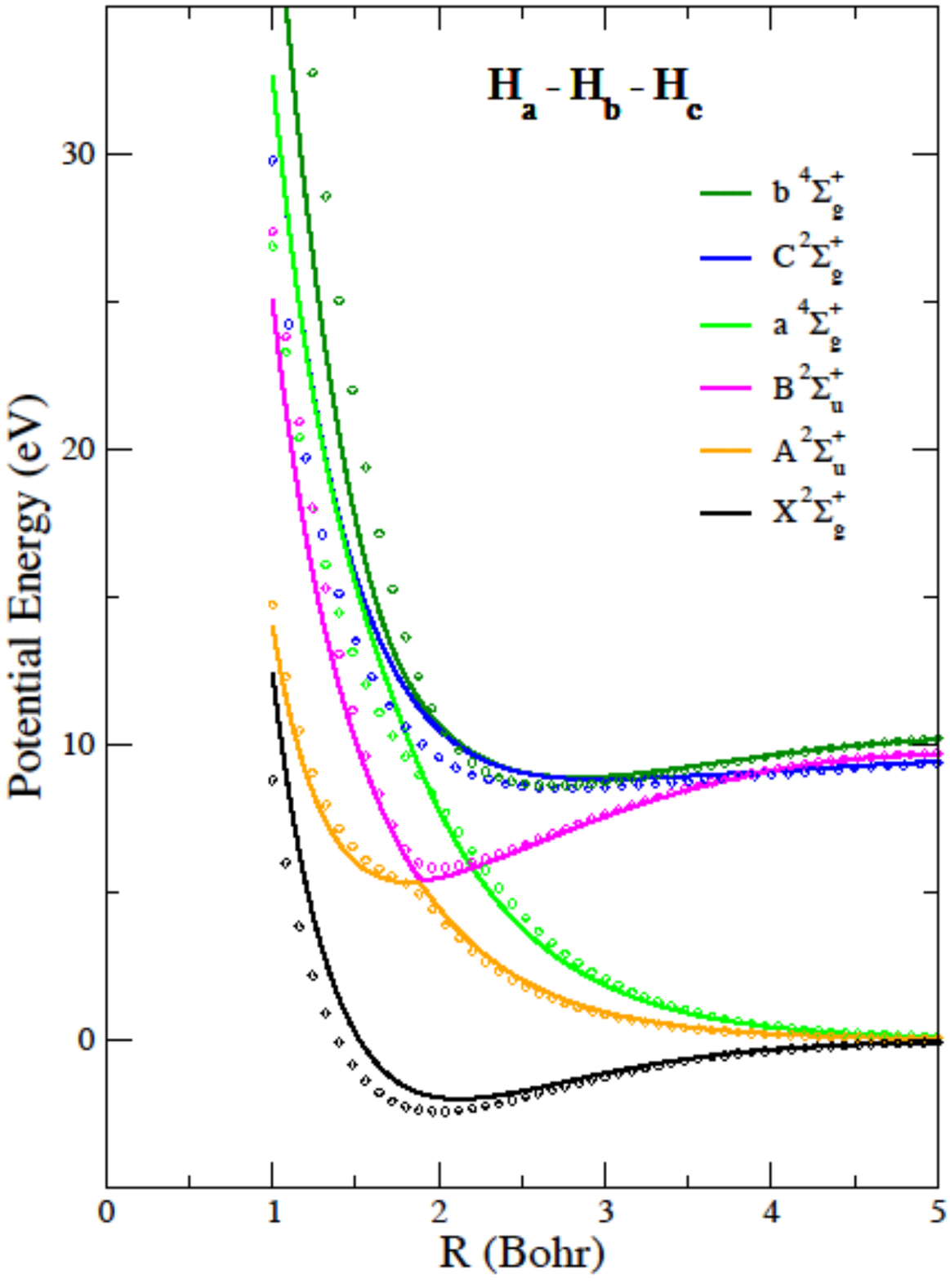
where α = a, b, c and i = 1 to 6 out of the N_{sp} = 64 molecular states

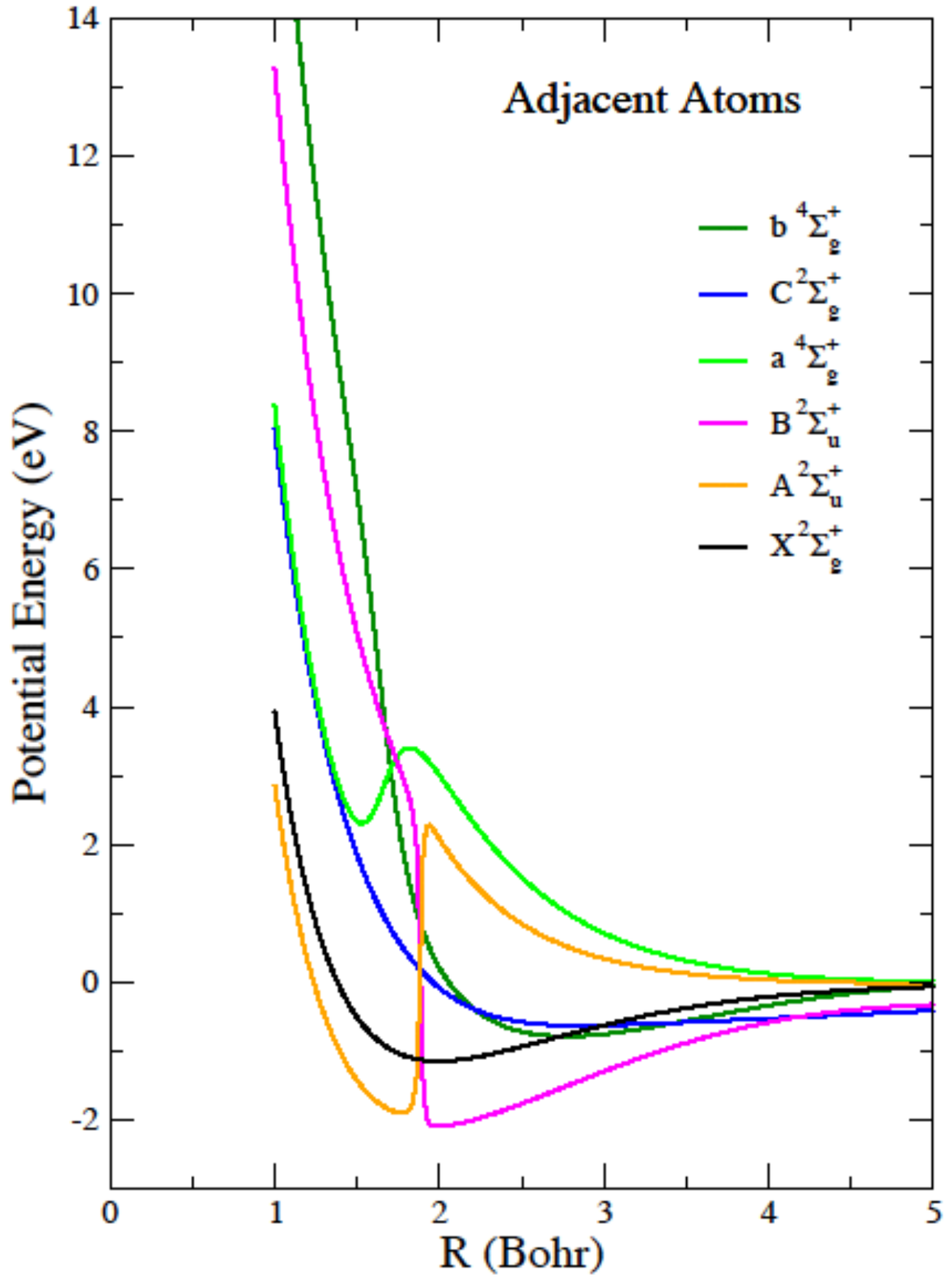
Three Collinear Hydrogen Atoms



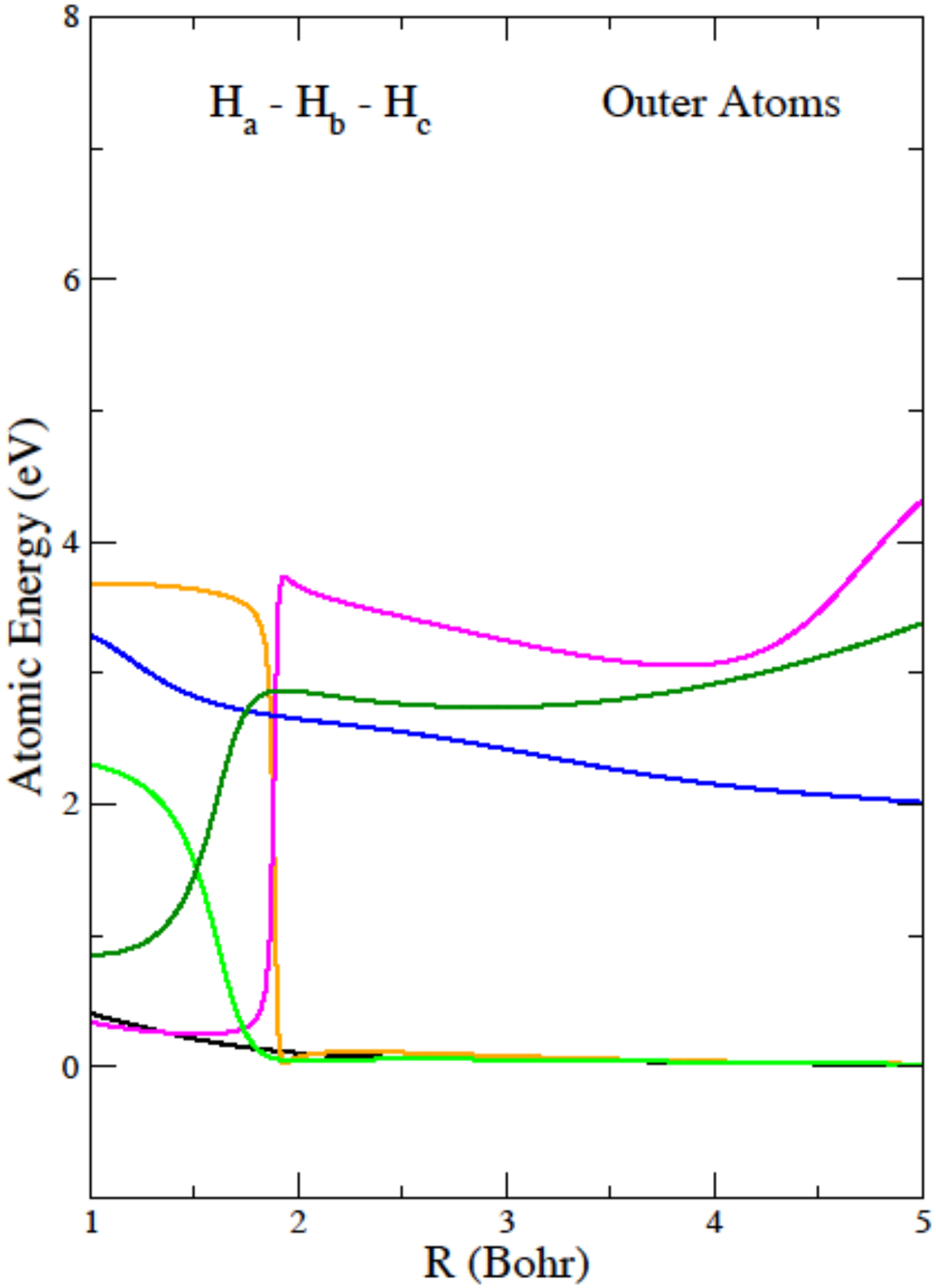


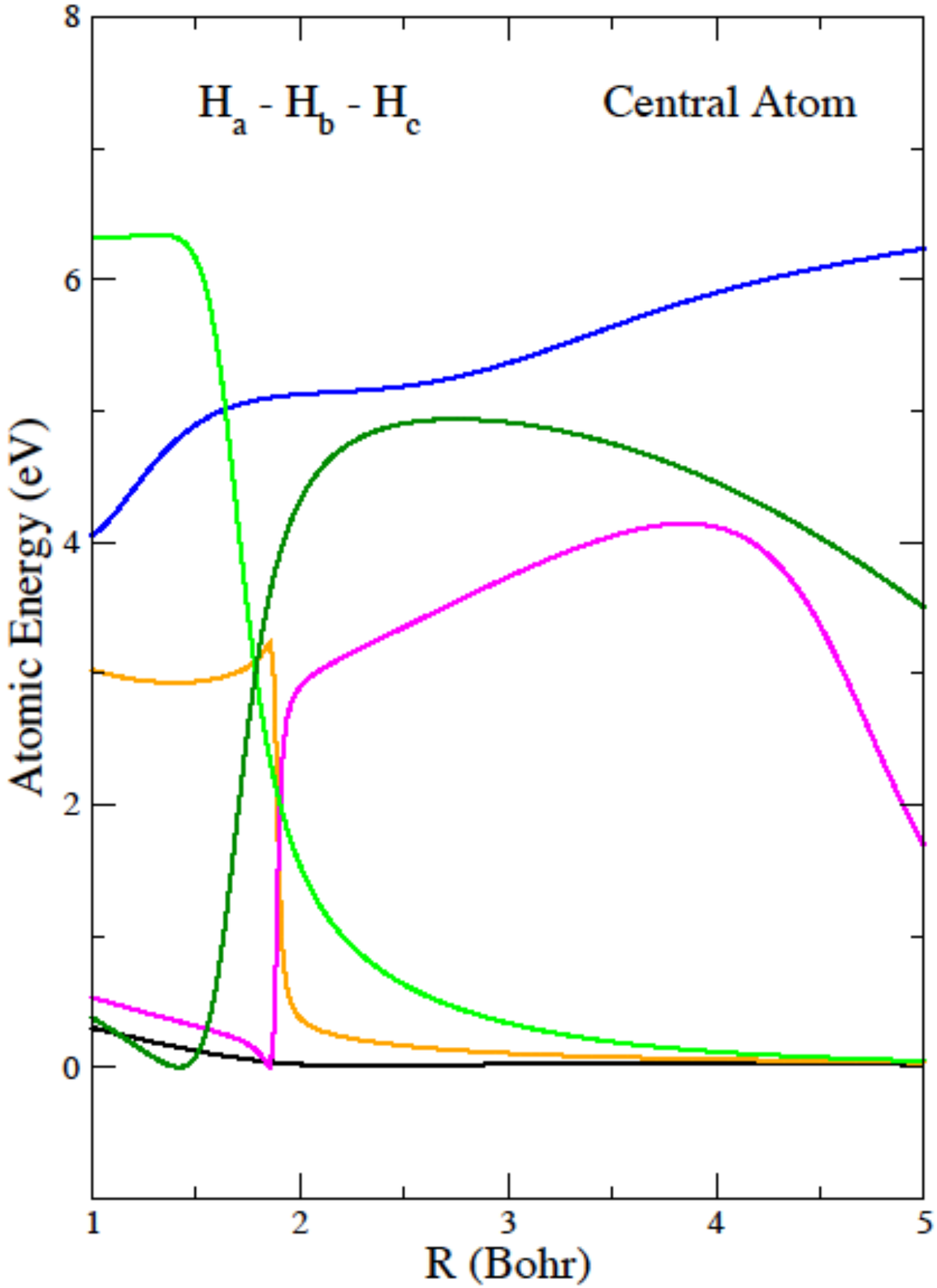
Low-lying potential energy curves and surfaces in collinear H_3



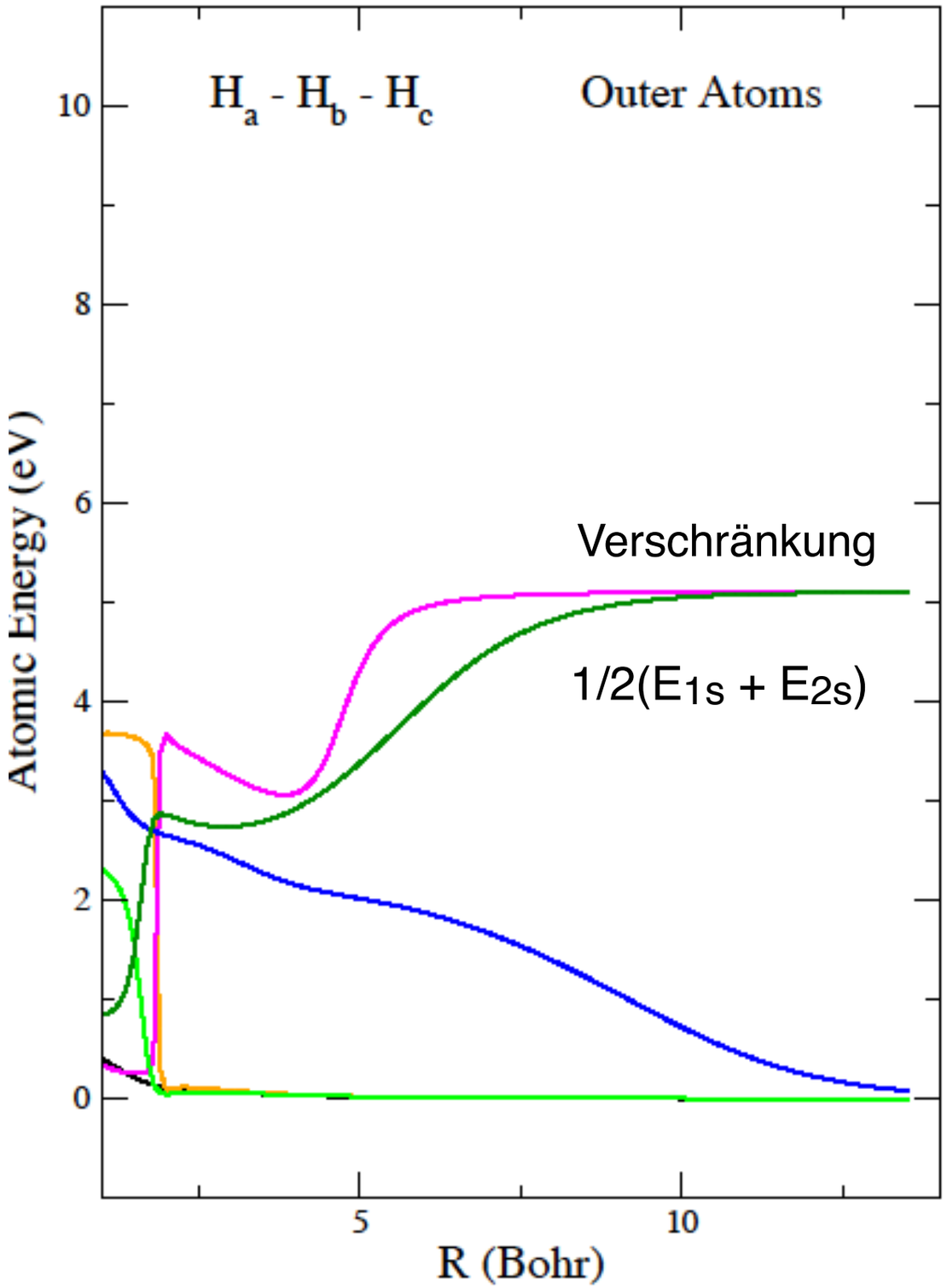


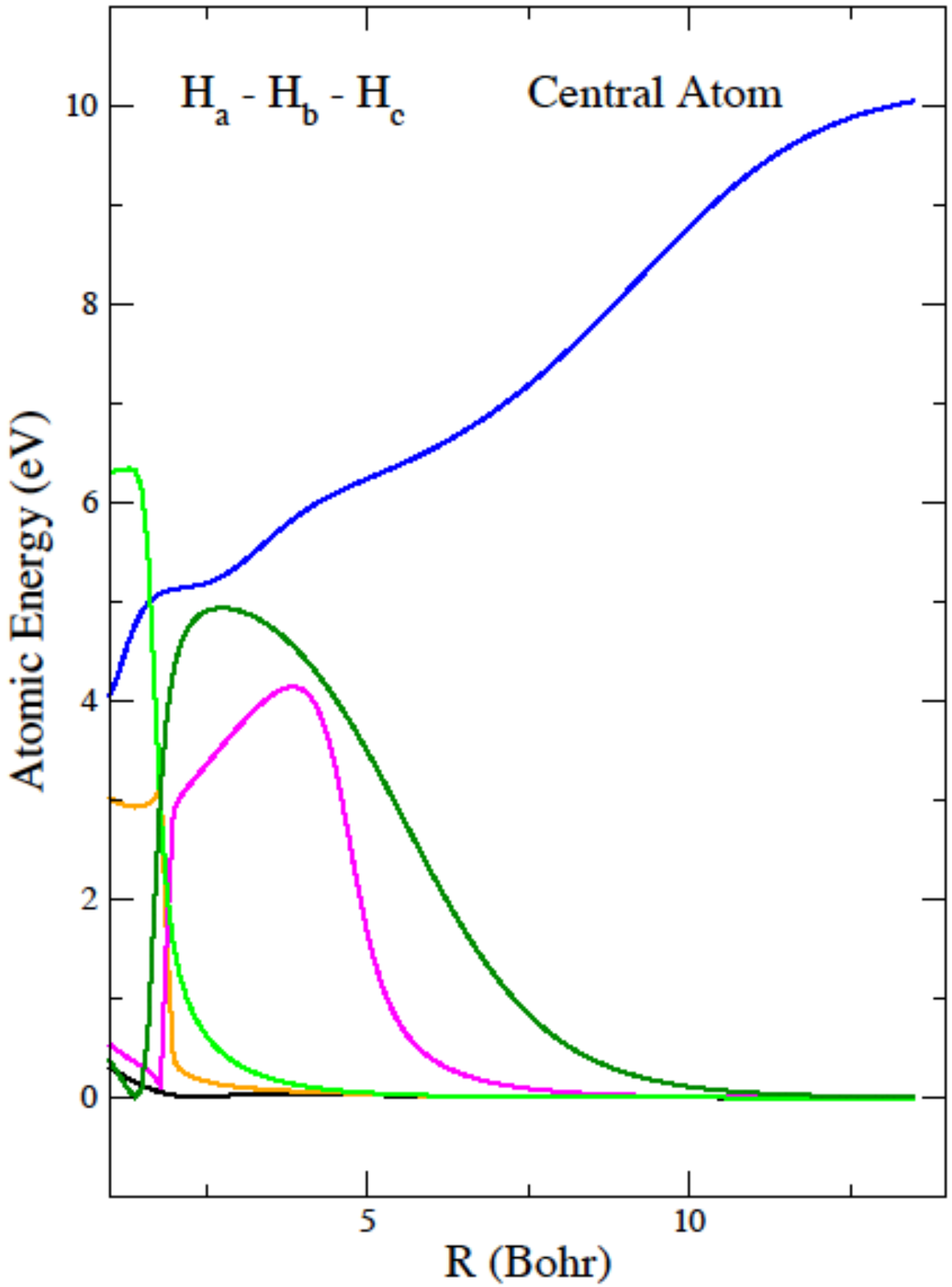
Potential energy curves and bonding potentials in symmetric collinear H_3 using four spin orbitals for each atom (1s,2s) giving a 64-term product basis



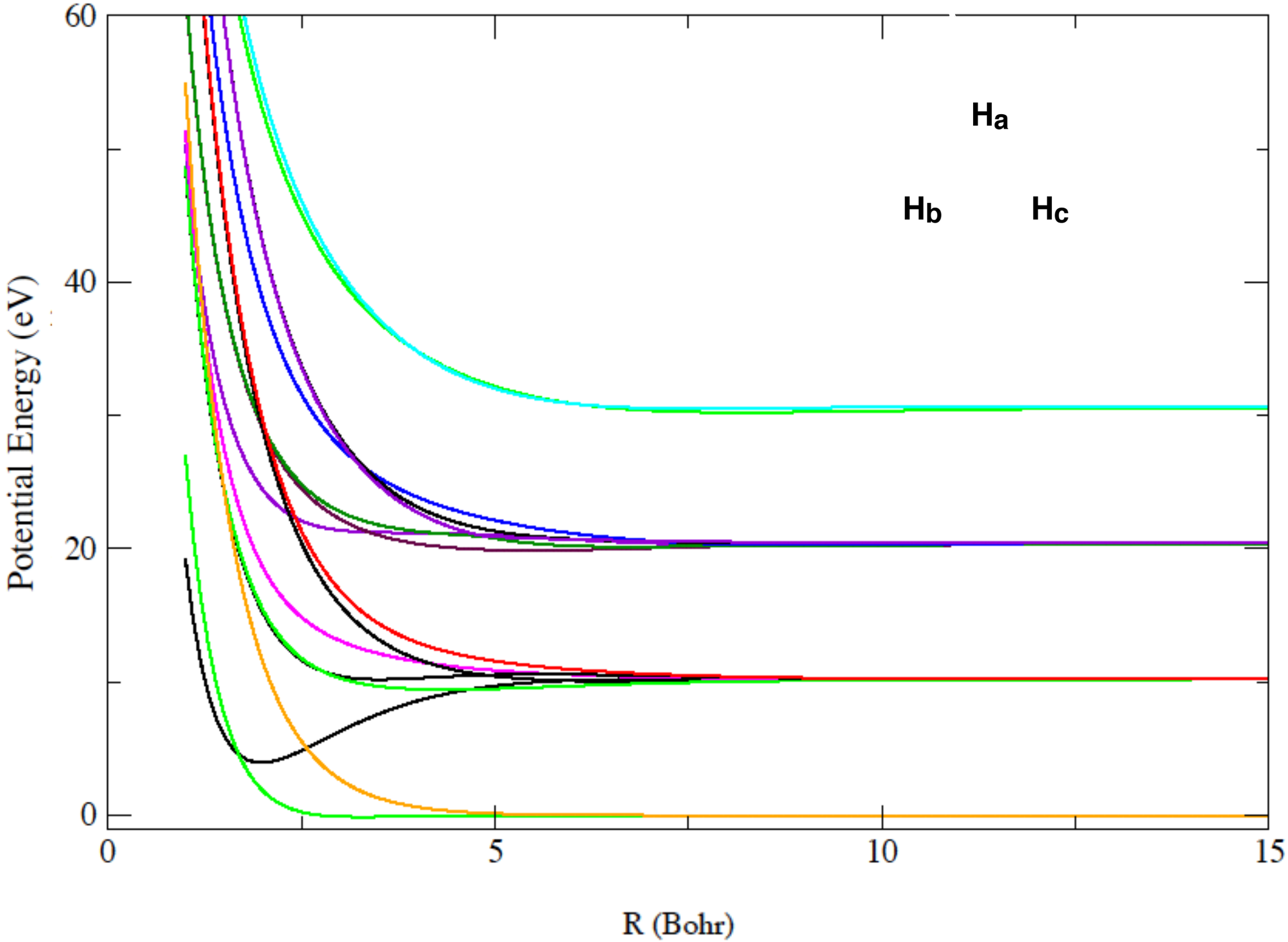


Outer- and central-atom promotion energies in 1s2s symmetric collinear H_3

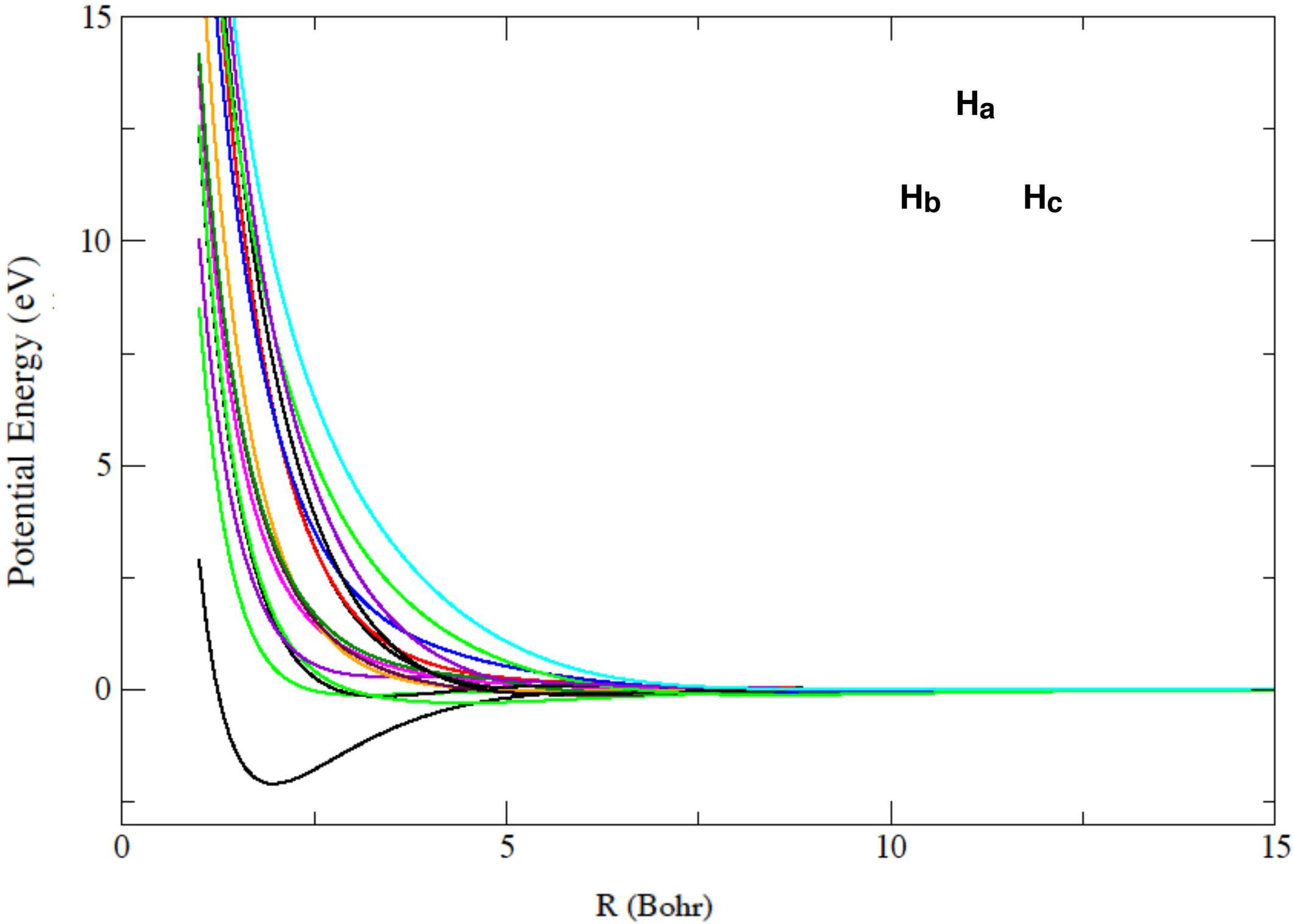




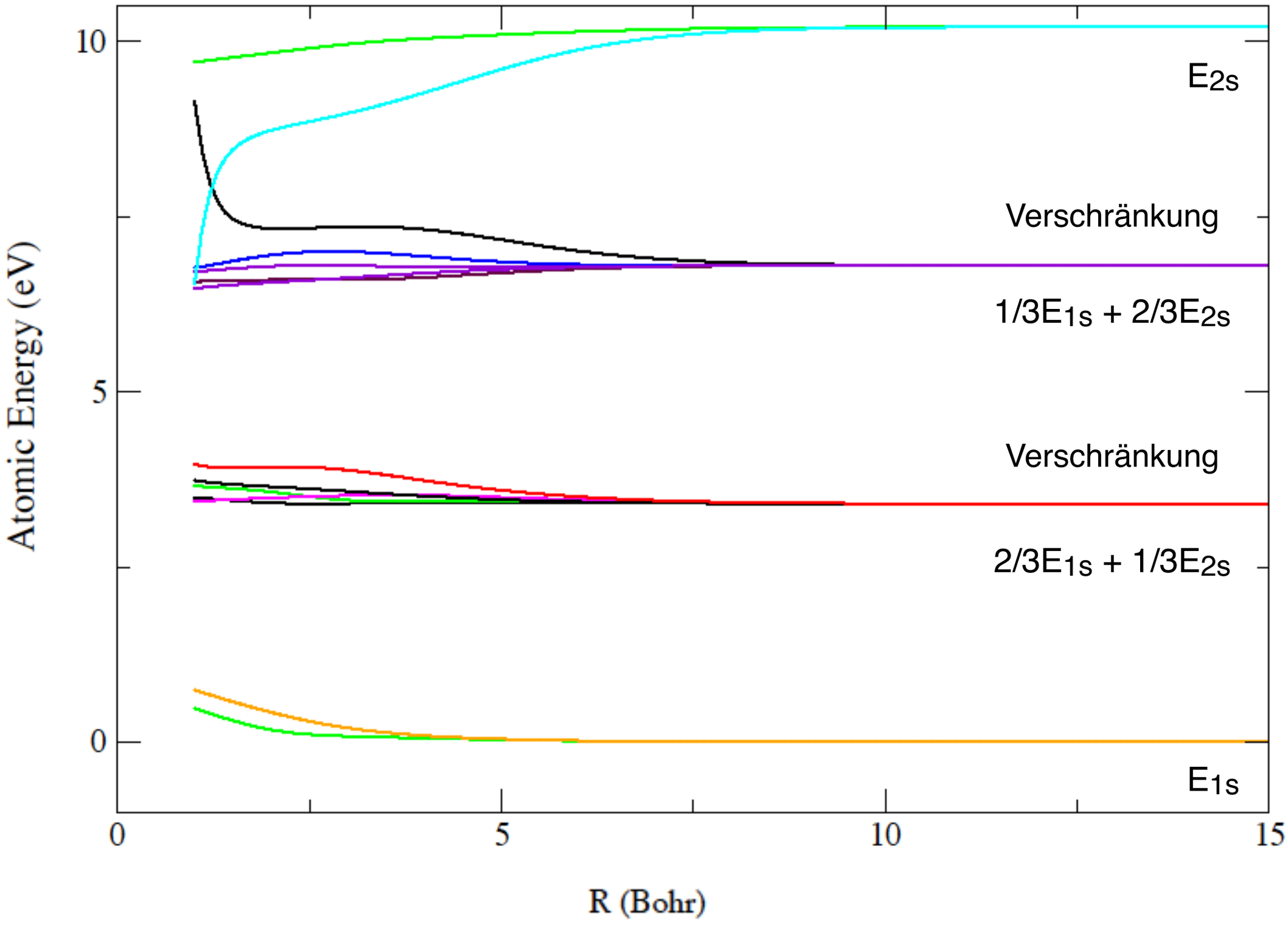
Outer- and central-atom promotion energies in 1s2s symmetric collinear H_3



Total potential energy curves in triangular D_{3h} 1s2s molecular H_3



Bonding energies in triangular D_{3h} 1s2s molecular H_3



Atomic (a,b,c) promotion energies in triangular D_{3h} 1s2s molecular H_3

Summary Remarks

An atomic representation is employed in which atoms are well defined in molecules

Potential energy surfaces are partitioned into atomic and bonding energy surfaces

Atomic and interaction energies are evaluated as conventional expectation values

Electronic charge is distributed through promotion into virtually excited atomic states

Implementation is provided for calculations in conventional finite subspaces

Illustrative applications describe atomic promotion and bonding in the H_3 molecule

Net bonding potential energies are seen to accommodate atomic promotion energies

Excited molecular eigenstates include “path-dependent” atomic entanglements

Measurement of atomic energies upon coherent dissociation can test the AIM concept

“…the chemical bond is not so simple as some people seem to think…”

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The most beautiful experience we can have is the mysterious.

Albert Einstein